

214 33 WO D2
(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 December 2000 (14.12.2000)

PCT

(10) International Publication Number
WO 00/75233 A1

- (51) International Patent Classification⁷: C08L 77/00, 77/02, 77/06 (74) Agent: VAN BORM, Werner, August, Hendrik, Maria; DSM Patents & Trademarks, P.O. Box 9, NL-6160 MA Geleen (NL).
- (21) International Application Number: PCT/NL00/00339
- (22) International Filing Date: 19 May 2000 (19.05.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
1012234 4 June 1999 (04.06.1999) NL
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- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— With international search report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HIGH-MOLECULAR POLYAMIDE COMPOSITION WITH IMPROVED FLOW BEHAVIOUR

(57) Abstract: The invention relates to a polyamide composition with improved flow behaviour that comprises at least 80-99.5 wt.% of a high-molecular polyamide and 0.5-20 wt.% of a polyamide oligomer that has a melting point that is higher than the melting point of the high-molecular polyamide, the amounts being relative to the total weight of the polyamide present in the composition. The high-molecular polyamide is preferably PA-6 or PA-4,6/6 copolymer and the polyamide oligomer is preferably chosen from the group comprising PA-6,6, PA-4,6, PA-4,6/6 copolyamide or copolyamides or mixtures thereof. The invention also relates to a process for improving the flow behaviour of a high-molecular polyamide composition by melt-mixing a high-molecular polyamide and a polyamide oligomer having a melting point that is higher than the melting point of the high-molecular polyamide at a melt temperature that is equal to or lower than the melting point of the polyamide oligomer and also a high-molecular polyamide composition obtainable with this process.

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HIGH-MOLECULAR POLYAMIDE COMPOSITION
WITH IMPROVED FLOW BEHAVIOUR

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The invention relates to a polyamide composition with improved flow behaviour that comprises at least 80-99.5 wt.% high-molecular polyamide and 0.5-
10 20 wt.% low-molecular polyamide, the amounts being relative to the total weight of the polyamide present in the composition.

Such a composition is known from JP-A-5214246 (Toray, 1992), which describes a composition
15 that comprises 100 parts by weight polyamide-6 and 0.001-10 parts by weight of a polyamide oligomer based on stearic acid, methylenediamine and sebacic acid, having a M_w of at most 5,000 and comprising modified end groups.

20 Said composition presents the drawback that the mechanical properties are not, or to an insufficient extent, retained after the addition of the polyamide oligomer according to JP-A-5214246. Another drawback is that modifying the polyamide end groups is
25 a laborious procedure and implies an additional process step in the preparation of the oligomer. Another drawback is that the polyamide oligomer is not commercially available, as a result of which the invention has had no commercial or large-scale
30 implementation up to now.

Obtaining a high-molecular polyamide composition with good flow behaviour and with the

typical polyamide properties being retained is of great importance for the purpose of obtaining films, fibres or moulded parts, in particular thin-walled moulded parts, that are obtained with the aid of the injection-moulding process. High-molecular polyamides generally have a high melt viscosity and poor flow behaviour. High-molecular polyamides do however have very good mechanical properties, in particular a high impact resistance, stiffness, deformation resistance and dimensional stability on heating, elongation at break and modulus of elasticity. For the purpose of improving the mechanical properties even further, in particular the stiffness or impact resistance the polyamide is often mixed with inorganic fillers such as glass fibres or impact modifiers. However, this leads to even further deterioration of the flow behaviour, so that it becomes difficult to injection-mould large or thin-walled moulded parts that also have an optically perfect surface, using for example glass-fibre-filled polyamide compositions.

An improvement in the flow behaviour is generally obtained by adding flow-promoting agents. Examples of flow-promoting agents mentioned in the literature are branched fluid crystalline oligoesters or oligoesteramides (EP-A-444295), low-molecular polyester (DE-A-4127720), polyolefinic waxes, modified with polar side chains (BE-A-820472) or salts of magnesium, zinc and aluminium (WO 97/19131).

The inventors have now surprisingly found that the drawbacks of the state of the art can be avoided and a high-molecular polyamide composition with good flow behaviour and with good mechanical properties can be obtained if this composition contains at least

0.5-20 wt.% low-molecular polyamide (a polyamide oligomer) having a melting point that is higher than the melting point of the high-molecular polyamide, the amount being relative to the polyamide's total weight.

- 5 The high-molecular polyamide has a different chemical composition than the polyamide oligomer in the composition according to the invention.

From WO 98/24836 is known a process for the production of a polyamide moulded part with improved
10 crystallisation behaviour from a polyamide composition containing 0.01-5 wt.% polyamide-4,6 and 99.99-95 wt.% of a polyamide having a melting point that is lower than that of polyamide-4,6. A composition containing a low-molecular polyamide 4,6 is not described, neither
15 is the advantage of any associated improved flow behaviour acknowledged.

Suitable polyamides, both with a high-molecular weight and with a low-molecular weight (oligomers), are all the polyamides known to a person
20 skilled in the art, comprising crystalline, semi-crystalline and amorphous polyamides. Examples of suitable polyamides according to the invention are aliphatic polyamides, for example PA-6, PA-11, PA-12, PA-4,6, PA-4,8, PA-4,10, PA-4,12, PA-6,6, PA-6,9, PA-
25 6,10, PA-6,12, PA-10,10, PA-12,12, PA-6/6,6-copolyamide, PA-6/12-copolyamide, PA-6/11-copolyamide, PA-6,6/11-copolyamide, PA-6,6/12-copolyamide, PA-6/6,10-copolyamide, PA-6,6/6,10-copolyamide, PA-4,6/6-copolyamide, PA-6/6,6/6,10-terpolyamide, and
30 copolyamides obtained from 1,4-cyclohexanedicarboxylic acid and 2,2,4- and 2,4,4-trimethylhexamethylene-diamine, aromatic polyamides, for example PA-6,I, PA-6,I/6,6-copolyamide, PA-6,T/6-copolyamide, PA-6,T/6-

copolyamide, PA-6,I/6,T-copolyamide, copolyamides obtained from terephthalic acid, 2,2,4- and 2,4,4-trimethylhexamethylenediamine, copolyamide obtained from isophthalic acid, laurinlactam and 3,5-dimethyl-4,4-diamino-dicyclohexylmethane, copolyamides obtained from isophthalic acid, azelaic acid and/or sebacic acid and 4,4-diaminodicyclohexylmethane, copolyamides obtained from caprolactam, isophthalic acid and/or terephthalic acid and 4,4-diaminodicyclohexylmethane, copolyamides obtained from caprolactam, isophthalic acid and/or terephthalic acid and isophoronodiamine, copolyamides obtained from isophthalic acid and/or terephthalic acid and/or other aromatic or aliphatic dicarboxylic acids, optionally alkyl-substituted hexamethylenediamine and alkyl-substituted 4,4-diaminodicyclohexylamine, or copolyamides or mixtures of the aforementioned polyamides.

Preferably polyamides are chosen from the group comprising PA-6, PA-6,6, PA-6,10, PA-4,6, PA-11, PA-12, PA-12,12, PA-6,I, PA-6,T/6,6-copolyamide, PA-6,T/6-copolyamide, PA-6/6,6-copolyamide, PA-4,6/6-copolyamide or mixtures or copolyamides of the aforementioned polyamides. More preferably PA-6, PA-6,6 or PA-4,6 is chosen, or mixtures or copolyamides thereof.

The polyamides in the composition according to the invention may optionally contain modified end groups, for example amine end groups modified with carboxylic acid.

The high-molecular polyamide has a weight-average molecular weight of at least 10,000 g/mol, preferably at least 15,000 g/mol, more preferably at least 20,000 g/mol.

The low-molecular polyamide has a weight-average molecular weight that is preferably lower than the "molecular weight between entanglements" of the high-molecular polymer. This "molecular weight between entanglements" is for example 5,000 g/mol in the case of PA-6. Preferably the weight average molecular weight is at most 5,000 g/mol, preferably at most 4,000 g/mol, more preferably at most 3,000 g/mol. The molecular weight may not be too low either, to avoid the risk of for example the glass transition temperature being lowered. Preferably the weight-average molecular weight is greater than approximately 1,000 g/mol.

Preferably, the composition comprises a high-molecular weight polyamide with a molecular weight of at least 10,000 g/mol and a low-molecular oligomer with a molecular weight of at most 5,000 g/mol.

More preferably, the composition comprises a high-molecular weight polyamide with a molecular weight of at least 15,000 g/mol and a low-molecular oligomer with a molecular weight of at most 4,000 g/mol.

The composition according to the invention comprises 0.5-20 wt.% oligomer, relative to the total amount of polyamide. The amount of oligomer can be chosen by a person skilled in the art within the given range, depending on the desired properties of the composition. Larger amounts of the oligomer result in a better flow behaviour, but too large amounts adversely affect the mechanical properties. Preferably an amount of 1-10 wt.% is chosen, relative to the total amount of polyamide.

The composition according to the invention preferably comprises a high-molecular polyamide, chosen from the group comprising PA-6, PA-6,6, PA-6,10, PA-4,6, PA-11, PA-12, PA-12,12, PA-6,I, PA-6,T/6,6-copolyamide, PA-6,T/6-copolyamide, PA-6/6,6-copolyamide, PA-4,6/6-copolyamide or copolyamides or mixtures thereof and a polyamide oligomer chosen from the group comprising PA-6,6, PA-4,6, PA-4,6/6-copolymer or copolyamides or mixtures thereof.

- 10 In the context of this application "PA-4,6" is understood to be a polyamide of which at least 50%, preferably at least 75%, more preferably at least 90%, consists of tetramethyleneadipamide units. PA-4,6 can be prepared through polycondensation of
- 15 tetramethylenediamine and adipic acid or an adduct thereof, optionally in the presence of other polyamide-forming monomers, for example ϵ -caprolactam, a different diamine, for example hexamethylenediamine or a different carboxylic acid, for example isophthalic
- 20 acid or cyclohexanedicarboxylic acid. Polyamide-4,6 and the preparation thereof are described in for example the Encyclopedia of Polymer Science and Engineering, Vol. 11, pp.315 ff (1988). The preparation process of PA-4,6 presents the advantage that it
- 25 consists of at least two steps, in which an oligomer having a $M_w = 1,000-5,000$ g/mol can easily be obtained. This oligomer can subsequently be after-condensed to obtain a high-molecular polyamide. PA-4,6 is commercially available under the trade name STANYL® and
- 30 is produced by DSM N.V., the Netherlands.

The composition according to the invention may also contain the usual additives, for example flame

retardants, fillers, release agents, lubricants and pigments. Preferably, the composition contains glass fibres. The low viscosity of the composition according to the invention can facilitate the dispersion of these
5 fillers as a result of the improved wetting.

The composition can be prepared in any way known to a person skilled in the art, for example by melt-mixing powder mixtures or granule mixtures, for example with the aid of an extruder. In a preferred
10 embodiment, the oligomer can be added to the melt of the high-molecular polyamide by means of a side-feeder mounted to the extruder.

It was surprisingly also found that the flow behaviour of the composition according to the
15 invention can be further improved by melt-mixing the polyamide components at a melt temperature that is equal to or lower than the melting point of the polyamide oligomer. This process offers the advantage that the composition according to the invention can be
20 used at the usual processing temperatures of high-molecular polyamides. The invention therefore also relates to a process for improving the flow behaviour of a high-molecular polyamide composition by melt-mixing a high-molecular polyamide and a polyamide
25 oligomer having a melting point that is higher than the melting point of the high-molecular polyamide, at a melt temperature that is equal to or lower than the melting point of the polyamide oligomer (but of course equal to or higher than the melting temperature of the
30 lowest melting polyamide in the composition, and a high-molecular polyamide composition obtained using the process according to the invention. The definitions of high-molecular weight polyamides and low-molecular

weight polyamides (oligomers) are the same as mentioned above for the composition according to our invention.

The invention will now be elucidated with reference to a few examples, but is not limited thereto.

Examples

Materials

10

High-molecular weight PA

Polyamide-6, $T_{\text{melt}} = 225\text{ }^{\circ}\text{C}$, $M_w = 18,500$, η_{rel} (formic acid) = 2.0, Akulon[®] K120 from DSM N.V., the Netherlands

15

Polyamide-6, $T_{\text{melt}} = 223\text{ }^{\circ}\text{C}$, $M_w = 25,500$, η_{rel} (formic acid) = 2.3, Akulon[®] K123 from DSM N.V., the Netherlands

Polyamide-6,6, $T_{\text{melt}} = 265\text{ }^{\circ}\text{C}$, $M_w = 23,000$, η_{rel} (formic acid) = 2.2, Akulon[®] S222 from DSM N.V., the

20

Netherlands

Glass fibre : length = 6 mm, diameter 1-14 μm

Oligomer PA-6,6, $M_w = 1,500$, $T_{\text{melt}} = 260^{\circ}\text{C}$

25

Oligomer PA-4,6, $M_w = 2,000$, $T_{\text{melt}} = 288^{\circ}\text{C}$

Determination of the physical properties

Modulus: determined at 23°C and 5 mm/min, according to

30

ISO 527

Tensile strength: determined at 23°C and 5 mm/min, according to ISO 527

Elongation at break: determined at 23°C and 5 mm/min, according to ISO 527

Flow behaviour: spiral flow length, determined by means of injection-moulding at 280°C and at an injection-

5 moulding pressure of $40 \cdot 10^5$ Pa.

Charpy N (notched) determined at 23°C according to ISO 179/1eA

Charpy UN (unnotched) determined at 23°C according to ISO 179/1eU

10 Surface: visual inspection of the surface of injection-moulded plates

Molecular weight: determined with the aid of standard GPC techniques

Melting point: determined with the aid of DSC (2nd run,

15 10°C/min.).

Examples I-VI and Comparative Examples A and B

A number of oligomers were mixed with high-molecular polyamide in a ZSK-30 twin-screw extruder

20 using a flat temperature profile of 250°C for PA-6 and 280 °C for PA-66, at a screw speed of 200 rpm and at a throughput of approximately 10 kg/hour. All the compositions contained 30 wt.% glass fibres, added via a side feed. The polymer melt was degassed at the end

25 of the extruder.

The results, presented in Table 1, show that the addition of an oligomer to a high-molecular polyamide leads to the formation of a high-molecular polyamide composition with good mechanical properties

30 and improved flow behaviour. Surprisingly, even better flow behaviour could be obtained than the flow behaviour of the composition containing a polyamide having the lower molecular weight (compare Comparative

Example A and for instance Example II). Surprisingly, melt-mixing the composition according to the invention at a temperature that is equal to or lower than the melting point of the oligomer (and of course above the melting point of the high-molecular polyamide) led to a composition with even more improved flow behaviour (compare Examples II and III and Examples V and VI). Surprisingly it was also found that the surface of injection-moulded plates having the composition according to the invention greatly improved relative to the surface of injection-moulded plates according to Comparative Example B.

Figure 1 shows the melt viscosity versus the shear rate in the event of capillary flow at 260°C of the compositions of Comparative Example A, Example III and Example VI. This shows that the pseudo-plastic behaviour, represented by the gradient of the curve, is not affected by the presence of oligomers in the composition as the entire curve has shifted to a lower viscosity. It may thus be stated that the oligomeric polyamides act as flow-promoting agents in the entire area that is relevant for injection-moulding applications.

Table 1: Properties of glass-fibre-filled (30 wt.%, relative to the composition's total weight) high-molecular PA-6 (K120 & K123) or PA-66 (S222) compositions containing different types of oligomers. The concentration of oligomers was calculated on the total amount of polyamide.

	Unit	A	B	C	I	II	III	IV	V	VI	VI
High-molecular polyamide		K120	K123	S222	K123						S222
Oligomer		-	-	-	PA-66			PA-46			PA-46
Conc. of oligomer	%	-	-	-	5	10	10	5	10	10	4
T-Compounding	C	250	250	280	265	265	250	280	280	250	280
T-Melt	C	263	276	301	281	280	260	294	295	264	296
Flow behaviour	mm	606	406	347	580	674	841	488	640	788	449
Modulus	GPa	9.42	9.04	8.77	9.27	9.46	9.82	9.11	9.54	10.35	9.11
Tensile strength	MPa	181	168	166	181	183	176	180	183	183	169
Elongation at break	%	3.35	4.47	4.5	3.17	2.80	2.38	3.45	2.57	2.47	3.3
Charpy N	kJ/m ²	11.6	13.4	8.7	11.0	11.0	10.7	11.2	11.0	10.5	7.8
Charpy UN	kJ/m ²	65.8	93.9	69.9	30.5	58.5	52.0	50.9	56.6	46.3	51.3
Surface		+	-	-	+	+	+	+	+	+	+

T-Compounding: the temperature set on the extruder.

T-Melt: the temperature measured in the melt.

Surface: + : good ; -: poor.

CLAIMS

1. Polyamide composition with improved flow
5 behaviour that comprises at least 80-99.5 wt.% of
a high-molecular polyamide and 0.5-20 wt.% of a
polyamide oligomer having a melting point that is
higher than the melting point of the high-
molecular polyamide, the amounts being relative
10 to the total weight of the polyamide present in
the composition.
2. Polyamide composition according to Claim 1,
characterised in that the average molecular
weight of the oligomer is at most 5,000 g/mol.
- 15 3. Polyamide composition according to Claim 2,
characterised in that the composition also
contains glass fibres.
4. Polyamide composition according to Claim 2 or
Claim 3, characterised in that the polyamides are
20 chosen from the group comprising PA-6, PA-6,6,
PA-6,10, PA-4,6, PA-11, PA-12, PA-12,12, PA-6,I,
PA-6,T/6,6-copolyamide, PA-6,T/6-copolyamide, PA-
6/6,6-copolyamide, PA-4,6/6-copolyamide or
copolyamides or mixtures thereof.
- 25 5. Polyamide composition according to Claim 4,
characterised in that the polyamides are chosen
from the group comprising PA-6, PA-6,6, PA-4,6,
PA-4,6/6 copolyamide or copolyamides or mixtures
thereof.
- 30 6. Polyamide composition according to any one of
Claims 1-5, characterised in that the amount of
low-molecular polyamide is 1-10 wt.%, relative to
the total amount of polyamide.

7. Polyamide composition according to any one of Claims 1-6, characterised in that the high-molecular polyamide is chosen from the group comprising PA-6, PA-6,6, PA-6,10, PA-4,6, PA-11, PA-12, PA-12,12, PA-6,I, PA-6,T/6,6-copolyamide, PA-6,T/6-copolyamide, PA-6/6,6-copolyamide, PA-4,6/6 copolyamide or copolyamides or mixtures thereof and the polyamide oligomer chosen from the group comprising PA-6,6, PA-4,6, PA-4,6/6-copolyamide or copolyamides or mixtures thereof.
8. Polyamide composition according to any one of Claims 1-6, characterised in that the high-molecular polyamide is PA-6 or PA-4,6/6 copolymer and the polyamide oligomer is chosen from the group comprising PA-6,6, PA-4,6, PA-4,6/6 copolyamide or copolyamides or mixtures thereof.
9. Process for improving the flow behaviour of a high-molecular polyamide composition by melt-mixing a high-molecular polyamide and a polyamide oligomer having a melting point that is higher than the melting point of the high-molecular polyamide at a melt temperature that is equal to or lower than the melting point of the polyamide oligomer.
10. High-molecular polyamide composition obtained using the process according to Claim 9.
11. Composition and process as described and elucidated with reference to the examples.

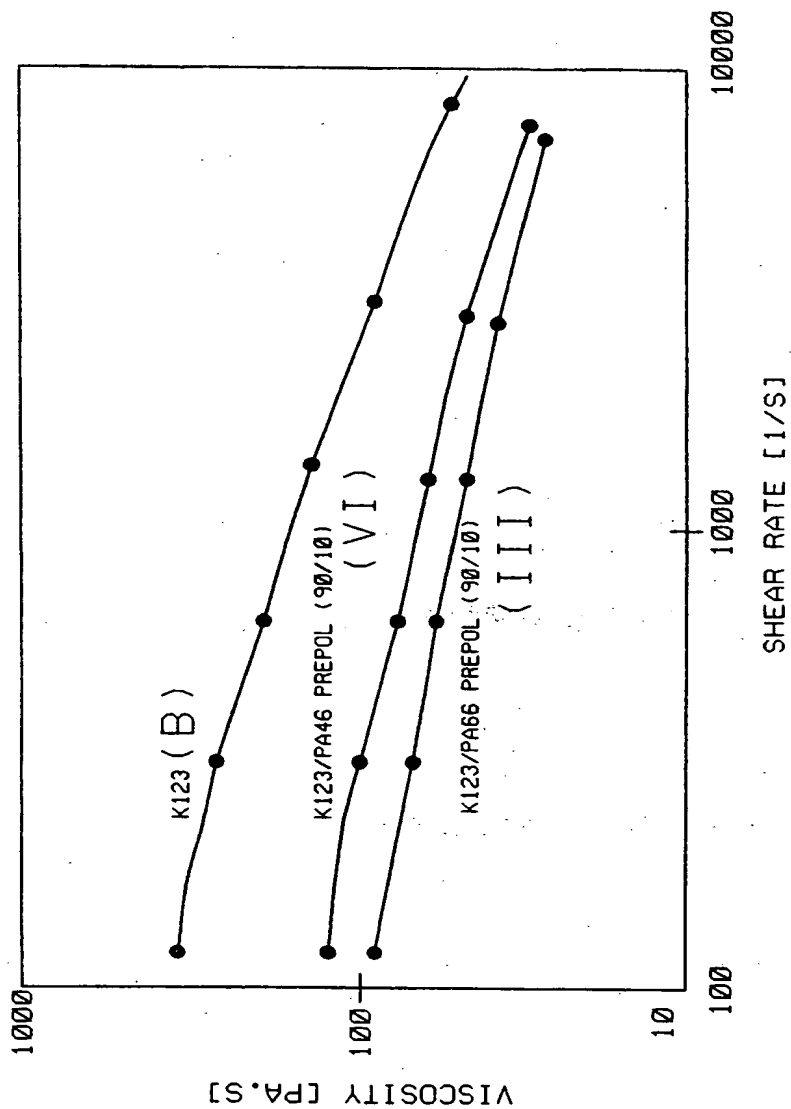


Figure 1/1

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Classification No.

PCT/NL 00/00339

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L77/00 C08L77/02 C08L77/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 199338 Derwent Publications Ltd., London, GB; Class A23, AN 1993-299806 XP002130383 & JP 05 214246 A (TORAY IND INC), 24 August 1993 (1993-08-24) cited in the application abstract	
A	EP 0 292 677 A (BOEING CO) 30 November 1988 (1988-11-30) page 3, line 15 -page 4, line 4	
A	WO 95 14059 A (ALLIED SIGNAL INC) 26 May 1995 (1995-05-26) page 5, line 30 -page 10, line 21	
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

25 August 2000

Date of mailing of the international search report

06/09/2000

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INTERNATIONAL SEARCH REPORT

Inter. Application No.

PCT/NL 00/00339

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 444 295 A (BAYER AG) 4 September 1991 (1991-09-04) cited in the application claim 1</p>	
A	<p>US 5 414 051 A (MASON CHARLES D. ET AL) 9 May 1995 (1995-05-09) column 2, line 6-59; claim 1</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. application No

PCT/NL 00/00339

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 5214246 A	24-08-1993	NONE	
EP 0292677 A	30-11-1988	US 4847333 A	11-07-1989
		CA 1319214 A	15-06-1993
		EP 0294555 A	14-12-1988
		IL 86317 A	25-05-1992
		JP 63305165 A	13-12-1988
		KR 9207527 B	05-09-1992
		US 4876328 A	24-10-1989
WO 9514059 A	26-05-1995	AU 693491 B	02-07-1998
		AU 1100795 A	06-06-1995
		CA 2176009 A	26-05-1995
		DE 69413247 D	15-10-1998
		DE 69413247 T	25-03-1999
		EP 0729490 A	04-09-1996
		JP 2744138 B	28-04-1998
		JP 9502478 T	11-03-1997
		US 5541267 A	30-07-1996
EP 0444295 A	04-09-1991	DE 4006403 A	05-09-1991
		JP 4227657 A	17-08-1992
US 5414051 A	09-05-1995	NONE	